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THE ADSORPTION AND DECOMPOSITION OF METHANOL ON ALUMINUM.(U)
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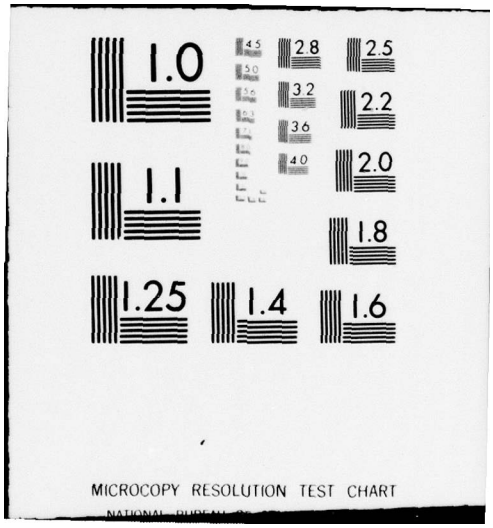
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J. W. Rogers, Jr. and J. M. White

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THE ADSORPTION AND DECOMPOSITION OF METHANOL ON ALUMINUM.

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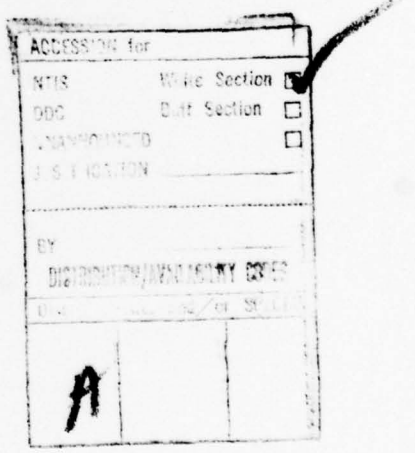
Abstract

The adsorption and thermal decomposition of CH_3OH on clean polycrystalline Al has been studied using UPS, XPS, and thermal desorption techniques in the temperature range 110-773 K. Molecular adsorption of CH_3OH occurs at 110 K; heating leads to a surface intermediate at ∿150 K which persists until 525 K. Beginning at 525 K CH_4, CO, CO_2, and H_2 are evolved and by 773 K the surface is oxidized. The nature of the surface intermediate is discussed.



I. Introduction

The decomposition of methanol (CH_3OH) on transition metals is an interesting reaction both from the standpoint of fundamental catalysis and fuel cell technology. CH_3OH being a simple organic molecule has a well understood gas phase UPS spectrum and is a likely candidate for UPS studies on metals. Being such, it has been studied on single crystal Ni,[1] W,[2,3] and Ru[4] as well as on polycrystalline Pd.[5] Some interesting studies on semiconductor surfaces, namely single crystal and powdered ZnO,[6,7] have also been published. CH_3OH decomposes to adsorbed CO and H_2 on most transition metals at room temperature. At low temperature (~80 - 120 K) CH_3OH can be condensed on transition metal and semiconductor surfaces. In the intermediate temperature range the surface species seem to depend upon the metal involved in the complex. No UPS work has been reported on non-transition metal/CH_3OH interactions. The purpose of this study was to see what effects the valence band of other types of metals, namely a free electron metal, would have on the adsorption and decomposition of CH_3OH in the temperature range 110-773 K.

II. Experimental Techniques

The sample was 1 cm^2 of 99.999% pure Al foil that could be resistively heated to 900 K and cooled to 110 K. The sample temperature was monitored using a chromel-alumel thermocouple. The Al was initially difficult to clean; 11 h of Ar ion bombardment at 0.2 milliwatt/cm^2 (5KV) at room temperature was required to remove the oxide layers as judged by AES.[8] Subsequent oxide layers acquired either by overnight adsorption of residual gases or by heating adsorbed CH_3OH were removed with < 5 minutes sputtering under the above conditions.

The kinetic energy distributions of the photoemitted electrons were measured using the double pass cylindrical mirror analyzer of a Physical Electronics Model 548 Electron Spectrometer. The analyzer was operated at a constant resolution of 0.4 eV (FWHM) for UPS and 0.8 eV for XPS. The sample was biased with a small negative voltage (1-3 volts) to facilitate accurate kinetic energy distribution widths for work function determination.[9]

The data were taken digitally using signal averaged pulse counting techniques and stored in a multi-channel analyzer. It could then be permanently transferred to a magnetic tape on a CDC 6600 computer. A 50 eV wide energy distribution was typically stored in 1024 channels of memory at a scan speed of 50 msec./channel.

The He resonance lamp used for production of HeII photons ($\hbar\omega$ = 40.8 eV) was differentially pumped; nonetheless, the system base pressure of 5×10^{-10} torr (6.65×10^{-8} Pa) increased to 1.2×10^{-8} torr of 99% He when the line-of-sight valve into the UHV was open for UPS measurements. AlKα x-rays ($\hbar\omega$ = 1486.6 eV) were used in XPS measurements.

Exposures of CH_3OH were accomplished using a calibrated, dynamically pumped doser system which was equipped with a multi-channel array (rather than the traditional nozzle) to eliminate flux gradients across the sample.[10] In

this manner, an exposure of 60 L (1L = 1 Langmuir = 10^{-6} torr-sec.) of very pure CH_3OH could be achieved in 5 minutes without raising the UHV system pressure above $10x10^{-10}$ torr.

Residual and desorbed gases were monitored with a UTI quadrupole mass spectrometer.

III. Results

HeII UPS spectra of CH_3OH adsorbed on clean Al at several temperatures and exposures are shown in Figure 1. Electron binding energies are referenced to E_F, the Fermi energy of Al. A and B were aligned by their respective Fermi levels, while C, D, and E were aligned with A and B by alignment of the peaks at 18 eV. This procedure will be addressed in Section IV.

Clean Al, shown in Figure 1A, exhibits a broad low intensity peak centered at ∿8 eV. This is due to the O(2p) resonance from a small quantity of oxygen which is adsorbed from residual gases within the UHV during the time necessary for an exposure. The work function of polycrystalline Al, measured from the width of the kinetic energy distribution is 4.3 eV. This agrees well with the average value of the work function for different faces of Al single crystals.[11]

Adsorption of 60L CH_3OH on Al at any temperature between 150-400 K produces a spectrum similar to that shown in B. The Fermi level of Al is clearly visible as well as two broad peaks at binding energies of 6.8 and 10.6 eV and a smaller peak at 18.0 eV.

Addition of another 100L CH_3OH to the 60L already shown in B produces a species responsible for curve C. This is saturation coverage at room temperature. The intensities of the peaks shown in B are increased but the intensity in the region of E_F is attenuated.

Figure 1D shows the molecular adsorption of 30L CH_3OH at 110 K. Four peaks are clearly resolved between 6 and 12 eV as well as a low intensity feature at ∿18 eV.

Saturation exposures of CH_3OH at 110 K are depicted in E with five well defined peaks in the region between 6-18 eV. Two low intensity features caused by HeII ($3s \rightarrow 1s$) photons ($\hbar\omega$ = 48.45 eV) are also present at ∿2.5 eV above and below E_F.

Figure 2 shows the O(1s) and Al(2p) regions of the XPS spectrum for various exposures of CH_3OH and O_2 at room temperature. Binding energies (E_{BE}) have been referenced to the Fermi energy of Al, by forcing the Al(2s) peak to 121.0 eV and making corresponding changes in the Al(2p) and O(1s) levels.

The Al(2p) resonance for clean Al is symmetrically centered (FWHM = 1.7 eV) at a binding energy of 73.3 eV. Adsorption of oxygen or CH_3OH produces a broad new feature of low intensity shifted $\sim$2.4 eV to higher binding energies.

At exposure of 250L CH_3OH produces a broad (FWHM = 3.3 eV) asymmetric peak in the O(1s) region centered at $\sim$533 eV, whereas the adsorption of 430L O_2 produces a symmetric peak (FWHM = 2.5 eV) at 532 eV.

Heating the species adsorbed in F to 620 K produces a transformation shown in G. Accompanying this transformation is the evolution of gaseous CO, CO_2, CH_4, and H_2,

IV. Discussion

Al, being a nearly free-electron metal, is particularly well suited to UPS studies because its valence band is essentially flat (it slowly varies as $(E_{KE})^{1/2}$ up to E_F) and difference spectra, with their inherent normalization problems, are unnecessary for the purposes of this study.

The five bands present in the gas phase UPS spectrum of CH_3OH have been assigned by Eland.[12] The first band, caused by ionization of the 2a" orbital, is due to the out-of-plane, non-bonding lone-pair electrons on oxygen. The third band which contains the unresolved 1a" and 6a' orbitals is due predominantly to the C-H bonding on the methyl group. The $7a'^{(-1)}$ transition involves an orbital which determines the HOC bond angle and the $5a'^{(-1)}$ transition is from the main bonding HOC orbital. The fifth band is due to the $4a'^{(-1)}$ transition which involves a weakly bonding core-like C(2s) orbital. These bands were assigned by comparing the gas phase UPS spectra of H_2O and CH_3OH. Several molecular orbital calculations of CH_3OH are in excellent agreement with and confirm these band assignments.[1,13]

There exists evidence that alcohols, aldehydes, and ketones all bond to metals end-on through the oxygen atom.[5] Assuming this to be the case for the CH_3OH/Al system, one would expect the $4a'^{(-1)}$ transition to be least likely to participate in a surface bond because, (1) it is not geometrically oriented to do so, and (2) it involves a core-like orbital. In addition, CH_3OH does not show any unusual relaxation/polarization shifts in the 4a' orbital.[14] We therefore chose this transition to align the curves in Figure 1 where no E_F was clearly present.

Adsorption at Low Temperature (110 K).

Condensation of CH_3OH at 110 K, this temperature being necessary to drop the equilibrium vapor pressure of CH_3OH into the 10^{-10} torr range, shows the

five peaks expected in this energy range from gas phase UPS studies on CH_3OH. The experimental gas phase vertical ionization energies, ε_i, from Robin and Kuebler[13] are displayed in Figure 1 after referencing these levels to the Fermi level of Al. This is accomplished by subtracting from the gas phase ionization potentials (I.P.'s) both the work function of the metal and the change in work function upon adsorption. $[E_{BE}(E_F = 0) = -(\varepsilon_i - \phi\ (\text{metal}) - \Delta\phi)]$. The extra-atomic relaxation/polarization energy defined by $\Delta E^R = E_{BE}^{gas}(E_F = 0) - E_{BE}^{adsorbed}(E_F = 0)$ was found to be 0.9 eV ± 0.1 and was constant for all valence orbitals. This indicates that the adsorbed species is indeed a condensed layer with no strong interaction between the condensate and the surface. The two low intensity peaks at ∿2.5 eV above and below E_F are due to excitation of the 2a" and 1a" - 6a' orbitals of condensed CH_3OH by HeII (3s → 1s) photons ($\hbar\omega$ = 48.45 eV).

Chemisorption of CH_3OH at 110 K is shown in Figure 1D. The relative intensities of the 7a' and 5a' orbitals have increased with respect to the 6a'/1a" orbitals as compared to the condensed phase. The large decrease in intensity and broadening of the 2a" peak is good evidence that bonding to the Al is occurring through the lone-pair electrons on oxygen as has been the case in general for alcohol-type molecules on metals.[5] The vibrational broadening of this level indicates a strong bonding interaction with the surface. The existence of four peaks in the valence region suggests that this species is molecularly chemisorbed without cleavage of the hydroxyl hydrogen. All valence orbitals are uniformly relaxed by 1.1 ± 0.1 eV except the 7a' and 5a' orbitals which undergo additional shifts of 0.5 and 0.2 eV respectively. These two orbitals are involved in COH bonding and would be expected to shift due to a steric distortion of the molecule caused by the close proximity of the O-H and O (lone-pair) - surface bond. Calculations and experiments have shown shifts of similar magnitude occur in the CH_3OH/Ni(111) system.[1]

Adsorption at Higher Temperature (150-400 K).

Adsorption of CH_3OH in the temperature range 150-400 K yields spectra similar to those shown in Figure 1B and 1C. They are significantly different from the low temperature work in two respects: (1) Only three peaks are clearly resolved instead of five, and (2) the two main peaks in the valence band are broader than their counterparts at low temperatures. A shoulder on the two peaks at 6.8 and 10.6 eV is also present. The species giving rise to these spectra was also found by Rubloff on Ni(111) in the temperature range of 160-300 K. It is clear that curve B derives from a chemisorbed species because the Fermi level has not been attenuated. The close resemblence of its three main features with features in curves D and E seem to indicate that a species with similar structure is responsible for both spectra. The assignment of the species in curves B and C to methoxide, i.e., the OH bond of the hydroxyl group has been cleaved, is consistent with the interpretation of our data offered in the following paragraphs. Assuming methoxide, one would expect the 5a' and 7a' obritals to be significantly effected since they involve the main COH bond and the angle determining COH bond. The 4a' [C(2s)] and 1a"/6a' [CH_3] orbitals would be least likely to participate in a surface bond during methoxide formation. The splitting between the 4a' and 1a"/6a' orbitals in curves D and E are identical whereas the splittings between the 1a"/6a' and 5a' or 7a' orbitals in B and E differ by as much as 0.9 eV. The ΔE^R for B is 0.5 ± 0.1 eV with the 5a' shifting an additional 0.3 eV, and the 2a" chemically shifting in the opposite direction of the other orbitals enough to completely offset the relaxation shift. This is not surprising since the bonding is expected to occur through the orbital containing the oxygen lone-pair electrons and shifts of this magnitude and direction (to higher BE) are well known.[5]

It is not unreasonable to expect methoxide since Al/methoxide complexes constitute a well known, stable class of compounds in inorganic chemistry; transition metal/methoxide complexes are known to exist for Ni, W, and Zn (among others) but have not been extensively studied.[15,16]

One must consider other oxygen containing intermediates which might produce the spectra shown in Figure 1. When the gas phase ionization potentials of formic acid, formaldehyde, and CO are referenced to the Fermi level of Al, and superimposed over the spectra in Figure 1, the agreement with the observed peaks is poor and indicates that these species are not formed.

The XPS and thermal desorption results provide further evidence for methoxide formation about 110 K. In Figure 2F the width and assymetry of the O(1s) resonance indicates that oxygen in at least two chemical environments is present when 250L of CH_3OH is adsorbed at room temperature. In order to calibrate where the oxygen transition from an Al/O interaction occurs as opposed to an Al/CH_3O interaction, a clean Al surface was exposed to 430L O_2 at room temperature which produces a coverage of $O \simeq 1$.[17] The result is shown in Figure 2E. The O(1s) peak is symmetric and centered at 532 eV. B and C show the effect of surface Al/CH_3O and surface Al/O interactions of the Al(2p) transition. In both cases, a broad, low intensity peak $\sim$2.4 eV higher in binding energy than the main Al(2p) transition is found.[18] It is impossible to determine if two surface species are responsible for the peak at 75.8 eV in Figure 2B due to the low intensity of this transition.

If CH_3OH is adsorbed as in F, and the temperature is increased to 620 K, there is a sharp onset of the evolution of CO, CO_2, CH_4, and H_2 into the gas phase, CO_2 being the main product. After cooling the surface back to room temperature curve G is obtained indicating the surface is left oxidized much as if O_2 were used as the oxidant. This can be seen by comparison of curves G and

E. After the thermal desorption the surface contains some residual carbon as monitored by UPS and AES results not shown. We consider CH_4 an unlikely gas phase product without the presence of surface methoxide. Aluminum methoxide (liquid phase) decomposes to CH_4, H_2, CO, and CH_3OCH_3 in the temperature range 573-653 K.[16] It should be emphasized that these are preliminary results and a complete discussion of the temperature stability of these complexes will be addressed in a forthcoming publication; we mention the thermal desorption work now only as further support for the notion that methoxide is formed. There is no evidence for desorption of CH_4 following adsorption of CH_3OH at 300 K on Ni, Ru, or W.[1,4,3] It is also apparent from comparison of E, G and F that the surface is partially oxidized at room temperature during the initial adsorption of CH_3OH in addition to the formation of a methoxide-like complex.

V. Conclusion

CH_3OH molecularly chemisorbs and can be condensed on clean polycrystalline Al at low temperatures (110 K). At higher temperature a similar but different surface species results with strong evidence indicating that this complex is surface methoxide. This complex decomposes to leave the surface partially oxidized beginning at 630 K. CO, CO_2, CH_3, and H_2 are simultaneously evolved in this process. A detailed study of the temperature dependence of these complexes will be published elsewhere.

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VI. Figure Captions

Figure 1: A) Clean Al, ϕ = 4.3 eV, T = 300 K. B) 60L CH_3OH, $\Delta\phi$ = -0.1 eV, T = 300K. C) 160L CH_3OH, $\Delta\phi$ = -0.5 eV, T = 300 K. D) 30L CH_3OH, $\Delta\phi$ = -0.1 eV, T = 110 K. E) 90L CH_3OH, $\Delta\phi$ = -1.2 eV, T = 110 K.

Figure 2: XPS spectra ($h\omega$ = 1486.6 eV) for CH_3OH and O_2 polycrystalline Al at 300 K. A) Clean Al. B) 250L CH_3OH. C) 430 L O_2. D) Clean Al. E) 430L O_2. F) 250L CH_3OH. G) 250L CH_3OH + heat to 620 K.

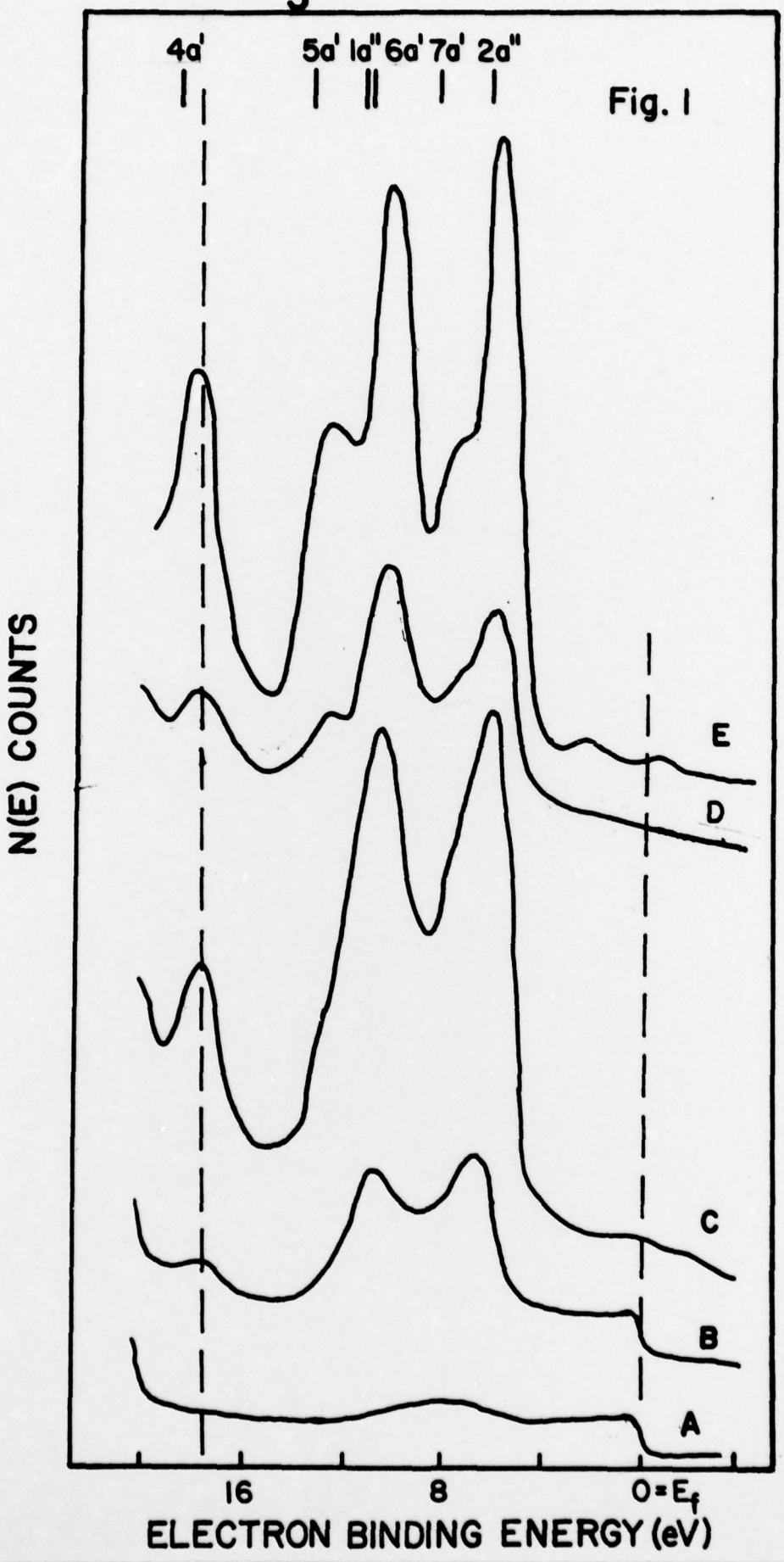
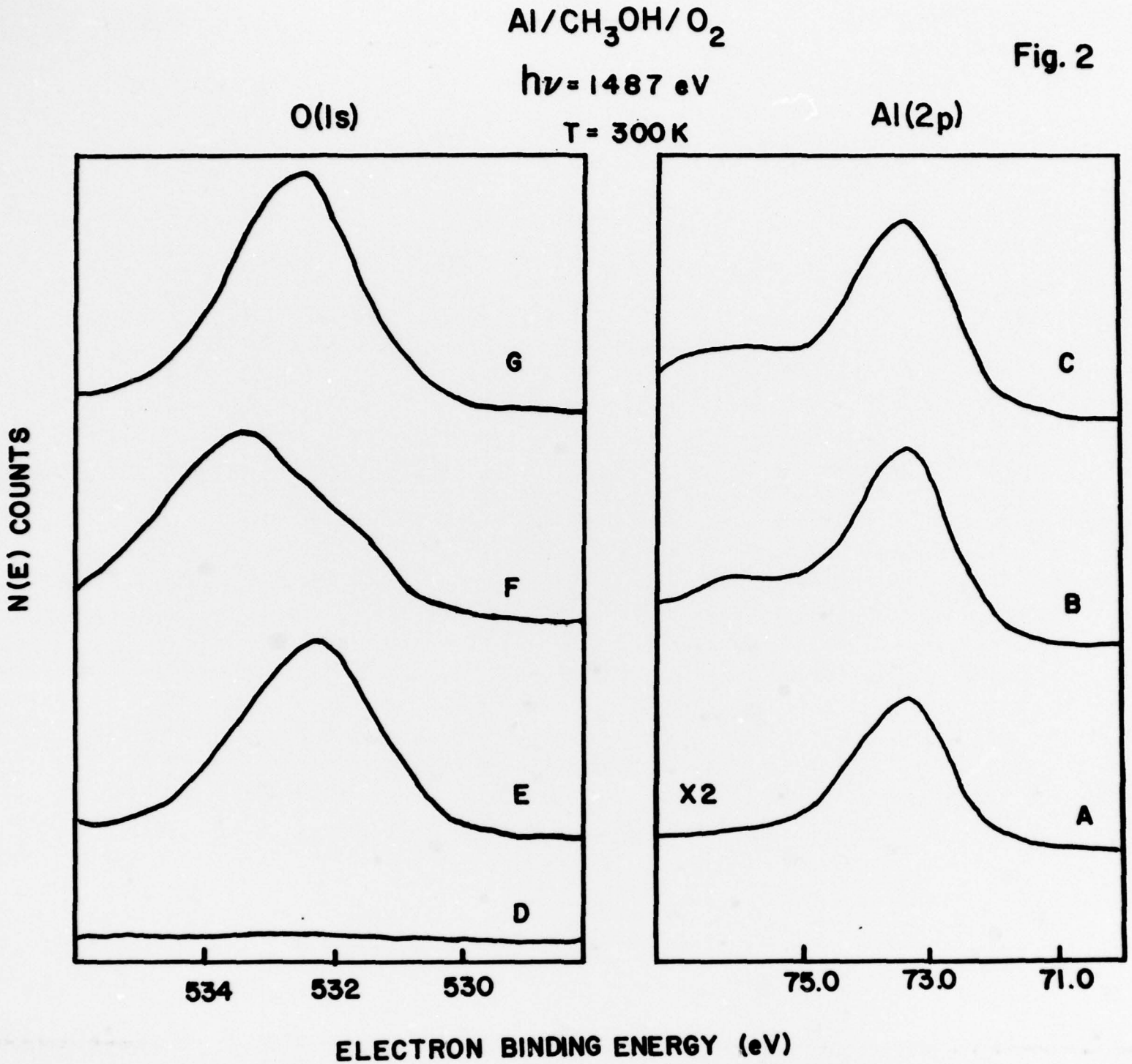

Al/CH3OH
hν=40.8
4a'
5a' 1a" 6a' 7a' 2a"
Fig. 1
N(E) COUNTS
E
D
C
B
A
16
8
0=Ef
ELECTRON BINDING ENERGY (eV)

Fig. 2


Al/CH3OH/O2
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T = 300 K
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Al(2p)
N(E) COUNTS
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E
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C
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A
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534
532
530
75.0
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71.0
ELECTRON BINDING ENERGY (eV)